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METHOD FOR COATING A SUBSTRATE
[VERFAHREN ZUM BESCHICHTEN EINES SUBSTRATES]

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The invention relates generally to coating of substrates in a vacuum, and in particular to a method for the coating of substrates which minimizes heat transport to the substrate, which can result in a deposition in which the chemistry of the vaporized material is reproduced.

The coating of many diverse types of materials by the known "physical vapor deposition" method has achieved widespread commercial importance. Such methods typically comprise the vaporization or sublimation of a coating material which is contained in a boat or crucible.

The material is heated by means such as resistance heaters or electron beams. For many materials it is advantageous for the deposition method to be carried out in a large vacuum, and typically this requires effective heating with electron beams.

Polymer materials are utilized with increasing frequency as replacement materials for glass in, for example, eyeglass lenses, windows, etc. Further, polymer materials are often used as replacement materials for metals, where the strength, durability, or hardness of the metals is not critical, but the object is decorative only. In such cases, the polymer plastic material is often coated with a thin (often 1000 Angstroms thin) layer of metal, in order to create the metallic appearance. In each of the above cases, the soft

plastic substrate consequently has a relatively low surface hardness and abrasion resistance in the end product. It is thus desirable to create a thin, hard, transparent coating from such glass-like material as for example silica (SiO_2) on such objects, in order to achieve a higher surface hardness and a greater abrasion resistance.

One of the difficulties in production of coatings from glass-like materials on plastic or metalized plastic substrates is the great sensitivity of such substrates to heat. Many known techniques to vaporize glass-like materials are per se unsuitable for coating of heat-sensitive materials owing to the great amount of heat which radiates from the vapor source. For example, a silica deposition can be achieved by direct vaporization of silica which is contained in a water-cooled copper crucible, in which the melted silica is bombarded with an electronic beam or beams. However the melt from which the silica is vaporized, typically creates a large region of heat radiation from which the substrate can be overheated.

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This happens because when a large amount of glass is heated, a large part of the material radiates heat energy, while only the surface vaporizes.

In the case of complex types of glass such as "Pyrex," for example, or of complex metal alloys, in which the components feature very diverse vapor pressures, it can be difficult to ensure that the chemistry of the vaporized material is reproduced in the deposition.

This is so because many material components consist of complex types of glass or complex compositions vaporize at different rates from a melt. This results in layering in the deposition, instead of a uniform composition.

Accordingly, it is the object of the invention that a method be provided for coating a heat-sensitive substrate with glass or glass-like materials, and that this method be carried out with a material with a complex composition, in which, the chemistry of the vaporized material is reproduced in the resulting deposition.

The invention is described in more detail below with reference to an exemplary embodiment and an attached drawing, wherein:

Figure 1 is a schematic perspective view of a device used to execute the method according to the invention and

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Figure 2 is a partial cross section along a vertical plane through the line 2-2 of Figure 1.

Very generally, the method according to the invention comprises an arrangement of the coating material in a configuration which in general is horizontally extended on a cooled holder. An electron beam or electron beams is (are) directed at a spatially specific region of the cooled holder, in order to create a vaporization zone in which the coating material to be vaporized is heated. A continuous relative movement between the coating material on the holder and the electron beam is created, in order to move the coating

material in the longitudinal direction into the vaporization zone. The energy of the electron beam or beams is selected so that basically the entire coating material is vaporized during its dwell time in the beam path.

The method according to the invention basically comprises continuous feeding of a material to be vaporized into the spatially determined vaporization zone at a selected, limited rate, and heating of same with the aid of an electron beam with adequate energy, in order basically to continuously vaporize the entire material in the vaporization zone. By restricting the size of the vaporization zone, the quantity of the heated material is minimized, with attendant minimization of the radiated energy. By rapid vaporization of the entire material in the vaporization zone, the chemistry of the deposition is basically identical to the chemistry of the material in the vaporization zone. Since only a small portion of the coating material is heated at any instant, and the entire heated material is vaporized, at a given time very little heated material exists to transmit heat to the substrate through radiation. Since the entire material basically is vaporized to the point of dryness, and

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no material to be cooled is left behind by cooling during drying, the net effect is a vaporization method which can create large quantities of vapor with very slight attendant heating of the substrate.

Figure 1 schematically illustrates an embodiment of a device which can be used to implement the invention. The device of Fig. 1 features a rotatable water-cooled copper crucible 11, which is used to carry the material to be vaporized. The crucible is secured to a rotatable shaft 13, which is driven by a suitable gear-drive mechanism 15. The upper surface of the crucible 11 is provided with an annular trough 17, whose cross section can be readily discerned in Fig. 2. The direction of rotation of the crucible is indicated by the arrow 19. The crucible is cooled by a suitable coolant, which flows in the channels 20 (Fig. 2).

The coating material to be vaporized is fed to the annular trough 17 in the crucible 11 with the help of the slide 21, which is extended from the lower end of a filling hopper 23. The coating material 25 can either be granulated as shown or ungranulated. The slide 21 can execute a shaking motion, in order to support the feed, and the feed rate can be regulated by changing the angle of the slide 21.

As soon as the material enters the annular trough 17, it is transported by rotation of the crucible 11 clockwise as viewed from above. An electron beam firing device 27, which is arranged under the level of the crucible, is used to produce an electron beam 29. The electron beam 29 is guided by suitable magnetic fields along a curved path of about 270° , so that it impinges on a spatially defined region 31 of the crucible, which

determines the vaporization zone. The electron beam firing device 27 can have any design, and does not need to produce the illustrated arcuate beam type. In US-PS No. 3,710,072, an electron beam firing device and a deflection system are shown and described which are modifiable in order to be incorporated in a system for execution of the method according to the invention.

The substrate to be coated, generally designated 33, features a rectangular flat configuration. However the substrate can have any configuration belonging to the state of the art and used in conventional coating systems, and is arranged directly over the vaporization zone.

It is evident that as a result of rotation of the crucible 11, the granulated coating material 25 placed in the annular trough 17, moves from the region in which it was first placed through an angle of around 90° into the vaporization zone. This separation naturally depends on the relative position of the vaporization zone with respect to the feed arrangement.

As mentioned above, the energy of the electron beam or beams, when a plurality of firing devices is used, is so great that basically the entire material vaporizes in the vaporization zone 31. With most materials vaporization is possible up to complete dryness. In some cases, however, a very thin film of the coating material remains as a coating in the trough 17. The cooling channels are shown in cross

section in Fig. 2. This assures that the electron beam does not melt or vaporize the crucible material itself, when the correct beam energy and cooling rates are selected.

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Heat flux measurements in a device which is similar to that shown in the drawing, and which operates in accordance with the method according to the invention, have shown that the temperature increase which a substrate experiences is only about half as great as when a conventional method is used. This applies not only to silica, but also to glass types with a more complex chemical structure. In the vaporization of silica or other corresponding glass compositions, a high concentration of silicon monoxide appears to exist in proximity to the vaporization zone. This material can be straw-colored in the deposited state, and is undesired in some coating cases.

Accordingly, it is advantageous to arrange the substrate at an adequate distance from the vaporization zone, in order to assure genuine reproduction of the chemistry of the coating material in the coating. Typically a distance between the vaporization zone and the substrate of more than 10.16 cm (4 inches) is necessary in order to prevent a disproportional silicon monoxide content in the deposited coating.

In the following, examples are mentioned in order to illustrate various relationships in which the method according to the invention can be carried out, as an aid in the choice of method parameters.

Example 1: A plurality of glass strips around 0.0624 cm thick x 2.54 cm wide x 7.62 cm long (around 1/16 inch thick x 1 inch wide x 3 inches long) was loaded into a substrate holder, so that they were located at various heights over the source in such a manner that each strip was continuously exposed to the vaporization source, that is, directly. A crucible arrangement was used which was similar to that illustrated in Fig. 1, and in which the trough 17 was charged with SiO₂ pieces in a layer with a width of 1.9 cm (3/4 inch) and thickness

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of around 0.254 cm (1/10 inch). Rotation at a speed of around one half rotation per minute is produced, and the pieces 25 are fed continuously along a slide 21 from the filling hopper 23 in Fig. 1, in order to fill and maintain this uniform layer in the trough. An electron beam with a power of 3 kW and a cross-sectional surface of around 0.125 cm x 2.54 cm (around 1/8 inch x 1 inch) was directed at the vaporization zone for a total time of 42 seconds, so that the pieces vaporized completely. The thickness of the coating produced on each strip is shown in the following table. These coating thicknesses should be understood as the maximum which can be formed with the specified beam energy.

Strip No.	Height over crucible, inches	Coating thickness, angstroms
1	4	150,000
2	8	65,000
3	12	25,000
4	14	25,000

Example 2: In a test similar to Example 1, pieces of modified aluminosilicate glass, known as Corning 7059, were arranged in a rotatable trough 17, and the following coatings were deposited on the glass strips in 35 seconds using a beam power of 3 kW and a rotational speed of 1/3 rpm:

Strip No.	Height over crucible, inches	Coating thickness, angstroms
1	4	110,000
2	8	45,000
3	12	22,000
4	14	22,000

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Example 3: Pieces which are obtained by crushing or milling of an ordinary plate glass used in glazing and supplied by the Libbey-Owens-Ford Company are arranged in the rotatable source and vaporized as in the prior examples for 45 seconds with a power of 3 kW and a rotation of 1/3 rpm with the following results:

Strip No.	Height over crucible, inches	Coating thickness, angstroms
1	4	175,000
2	8	60,000
3	12	20,000
4	14	20,000

Example 4: As proof of a low heat development from the source, the following heat-sensitive plastic substrates were arranged 15.56 cm (14 inches) over the water-cooled rotating trough 17 at the same time:

1 Polycarbonate piece with a thickness of 0.635 cm (1/4 inch)	Obtainable under the trade name Lexan from the General Electric Co.
1 Polycarbonate piece with a thickness of 0.476 cm (3/16 inch)	
1 Polymethyl methacrylic acid ester piece with a thickness of 0.635 cm (1/4 inch)	Obtainable under the trade name Acrylite from the American Cyanamide Co.
1 Acrylonitrile butadiene-styrene piece, gray	Generally known as ABS
1 Acrylonitrile butadiene-styrene, black	

After deposition of silica for two minutes at a beam power of 2 kW and a rotational speed of around 1/2 rpm, a hard, transparent coating from silica is formed with a thickness of around 60,000 Angstroms on each plastic specimen without damaging the specimen as a result of temperature change.

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Example 5: An arrangement was used which was similar to that of Example 4, whereby SiO₂ pieces were used. A plastic lens which was made from a 0.169 cm thick (1/16 inch) polycarbonate was coated with 60,000 Angstroms of silica at 2 kW for two minutes, with a rotation of about 1/2 rpm.

Example 6: Aluminum and tungsten wires were arranged parallel to one another on the circumference of a rotatable cooled holder, similar to that shown in Fig. 1. A collection strip was secured in

the evacuated chamber, and a beam power of 3 kW was used, in order to vaporize both wires. With a fixed state of vaporization and rotation, the aluminum would clump together with the tungsten wire and fuse with it, and the alloy itself and the combined wires would vaporize to dryness. This resulted in a uniform alloy coating of tungsten and aluminum on the strip. Accordingly, aluminum and tungsten, which feature vapor pressure differences of 10^{12} , were vaporized in order to form an alloy which previously was not possible from vaporization from a single source.

Example 7: A finely divided mixture of one part boroxide and three parts melted silica was vaporized according to the invention at an electron beam power of 1.8 kW on a glass collection strip. The resulting vitreous transparent film was a mixture of the vaporization material, and analysis revealed the presence of a duplicate of the vaporization chemistry.

From this it is evident that the invention creates an improved method to coat a substrate in an evacuated environment. Heat-sensitive substrates can be successfully coated with glass-like materials, and complex alloys can also be easily formed,

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which feature components with very different vapor pressures.

Hence a method for the coating of a substrate by condensation of vapor on same in an evacuated environment is created. The coating material is vaporized from a cooled coating material holder, which is

moved continuously forward with respect to the impinging electron beam. The beam energy is correlated to the rate by which the coating material is presented to the beam by the advancing material holder, in order to assure that the entire coating material is vaporized during its dwell time in the beam.

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Claims

1. A method for coating a substrate by vacuum vaporization and condensation, characterized in that an electron beam is directed onto a spatially defined region of a cooled support for the material to be vaporized, that a relative movement between the beam and the support is created so that the spatially defined region advances gradually along the surface of the support, that a coating material to be vaporized is positioned on the support in the path to be covered by the beam, that the advancing speed of the beam transversely over the surface and the beam energy are correlated in order to assure that basically the entire coating material entering the beam path is vaporized during its dwell time in the beam, and that the substrate to be coated is positioned in the path of the produced vapors, causing a coating of the vaporized material to be deposited on the substrate.

2. Method according to Claim 1, characterized in that the beam is stationary and the support for the material to be vaporized is moved

forward with respect to the beam, in order to transport the material to be vaporized into the beam at a preset uniform rate.

3. Method in accordance with Claim 1, characterized in that the material to be vaporized is formed from finely divided particles, which are uniformly distributed on the support in the path passed over by the beam.

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4. Method in accordance with Claim 1, characterized in that the support for the material to be vaporized is cooled to the extent that is required in order to prevent significant transfer of beam energy from the support to the substrate.

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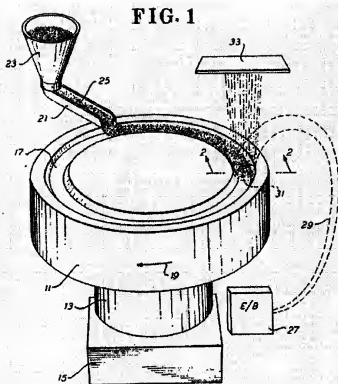


Figure 1

FIG. 2

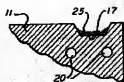


Figure 2